ADSORPTION OF ASYMMETRIC POLAR COMPOUNDS ON OIL SHALE AND ITS SPECIAL FORM

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Abstract
Adsorption of two different asymmetric polar organic compounds - TEBA (benzyltriethylammonium chloride) and Supragil WP (sodium diisopropyl naphthyl sulfonate)- on oil shale andits composite was investigated. These anthropogenic pollutants are similar to surfactants therefore they are frequently used in different products and could be transformed into environmental contaminants. In order to find more efficientandmanageable form of oil shale, we compared the adsorption of oil shale powder to oil shale ina composite form (oil shale-alginate). According to the comparison, the amount of TEBA adsorbedon oil shale in composite form was lessthan on powder, while that of Supragil WP was higher. These results could be explained by the differentliquid-solid ratioand by the different diffusion rate through the alginate.

Introduction
In Hungary, the oil shale is a unique rock, which is present in a large amount. Oil shale originatesfrom the biomass of algae accumulated in the volcanic craters over 4 to 5 million years.This oil shale is widely used as a soil-ameliorating agent because of its special microelement and organic contents and low price. The organic material content is between 5 to 50 % and consists of mainly kerogen [1]. Recently, usage of oil shale to eliminate chemical pollutants is an emerging topic [1-3]. This oil shale is easily crumbling, which hindersits easy and routine applicability.
Alginate is an anionic polysaccharide copolymer, it derives from cell wall of brown algae, consists of β-D-mannuronate and α-L-guluronate. In the literature, alginate is a new material as a forming, immobilizing agent [4-5]. Alginate has also been used as an environmental pollutant removal agent [6]. The disadvantage of application of alginate is its relatively high price. The combination with a lower-cost adsorbent can result in a new material, which might be useful to eliminate hazardous chemicals.
Supragil WP (Figure 1, left) is an anionic chemical, which is widely used as a dispersant, especially in pesticides.TEBA is a popular cationic phase transfer catalyst at organic chemical syntheses (Figure 1,right).The structure of both chemicals is similar to surfactants, therefore they can be considered as asymmetric polar compounds[7].

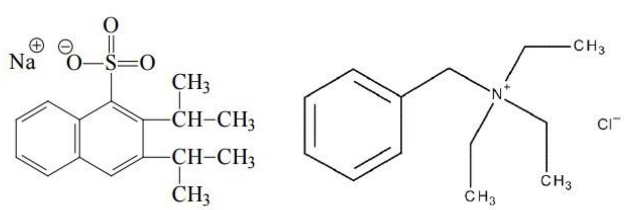

Figure 1. Chemical structures of Supragil WP (left) and TEBA (right)

Due to these facts, these two asymmetric polar compounds (Supragil WP and TEBA) might be potential environmental pollutants when they get into the soil or natural waters.
The aim of this present work is to form the oil shale in a practical form, whose adsorption is similarly efficient as the oil shale powder.In order to achieve our aim,we performedadsorption experiments on oil shale powder and oil shale composite, and compared their adsorption capacities.

Experimental
Oil shale sample originated from Pula (Hungary) and was milled: ∅<0.8 mm.
Sodium alginate was purchased from Sigma-Aldrich Co., Supragil WP was obtained from Rhodia Geronazzo Spa., TEBA originated from Merck KGaA. and calcium chloride was purchased from Lach-Ner, s.r.o. All chemicals were used without further purification.
UV-VIS measurements were performed on a Varian Cary 50 UV-VIS spectrophotometer,pH was determined with a Radelkis combination pH electrode.
The nonlinear least square fitting procedure of the Origin scientific graphing and analysis software was utilized, using Levenberg-Marquardt algorithm.

Preparation of alginate beads
Alginate beads were prepared according to the literature [4]. A solution of 2.5 % (w/v)concentration was prepared by dissolution of sodium alginate in deionized water. The obtained mixture was dropped into 0.2 mol/L $CaCl_2$ solution and alginate beads were formed (∅: ~ 5 – 6 mm). After standing in the gelation media overnight, the beads were filtered out and washed with deionized water.

Preparation of oil shale composite beads
According to the above described procedure, sodium alginate mixture was prepared. This solution was mixed with the swollen oil shale,using 8 : 1 mass ratio of oil shale and sodium alginate. This suspension was added dropwise into 0.2 mol/L $CaCl_2$ solution and oil shale composite beads were formed (∅: ~ 5 – 8 mm). The post-treatment is identical with that applied in the case of alginate beads.

Adsorption on oil shale powder
The adsorption experiments were performed in 250 mL stoppered Erlenmeyer flasks. 5 g of oil shale powder was weighed into the flask and was left to swell in 5 mL water overnight at 25 °C. Different concentrations of Supragil WP (from 50 to 500 μmol/L) or TEBA (from 2 to 20 mmol/L) solutions were prepared with 0.01 mol/L $CaCl_2$(pH=7.4).50-50 mL of these solutions were transferred to the swollen oil shale samples. The suspension was then shaken and left to stand for 24 hours for equilibration at 25 °C. Then approximately 2 mL of the supernatant was transferred into an Eppendorf tube and was centrifuged at rpm = 15000 for 20 minutes for perfect separation of the supernatant and oil shale powder. After the centrifugation, the supernatant was measured by UV-VIS spectrophotometer and the concentration was determined.

Adsorption on alginate beads and oil shale composite beads
The procedure to measure the adsorption on alginate and oil shale composite was almost the same

as in the case of the adsorption on oil shale powder. In this case,instead of oil shale powder,the alginate beads or oil shale composite beads were weighed. Everyoil shale composite bead contained 5 g of oil shale powder. The alginate content of the weighed oil shale composite beads was equal to the weighed alginate beads at these adsorption experiments.

All samples were in triplicate. The UV-VIS absorbance of the blank sample (c_0= 0 mol/L) was subtracted.

Results and discussion

The adsorption isotherms for Supragil WP and TEBA on oil shale powder and oil shale composite were analyzed in terms of Freundlich isotherm equation well:

$$q_e = K_F \cdot c_e^n$$

where q_e is the adsorption capacity at equilibrium, mol of solute adsorbed per gram of adsorbent (mol/g);c_e is the equilibrium solution concentration (mol/L);K_F($L^n/(mol^{(n-1)}\cdot g)$) and$n$ are constants that characterize the adsorption capacity of adsorbent of solute.

The equations were fitted to the obtained data, the calculated parameters and the statistical indicators of the overall goodness of fitting (R^2) were between 0.98144 and 1.

The adsorbed amount of the solute was calculated according to the following equation:

$$q = \frac{V \cdot (c_0 - c)}{m}$$

where q is adsorption capacity at equilibrium (mol/g); V is the volume of the equilibriumsolution (0.05 L); c_0 and c are the initial and the equilibrium concentrations of the solute (mol/L); m is the weighed amount of the dry adsorbent (g).

The obtained adsorption isotherms are shown in Figure 2.

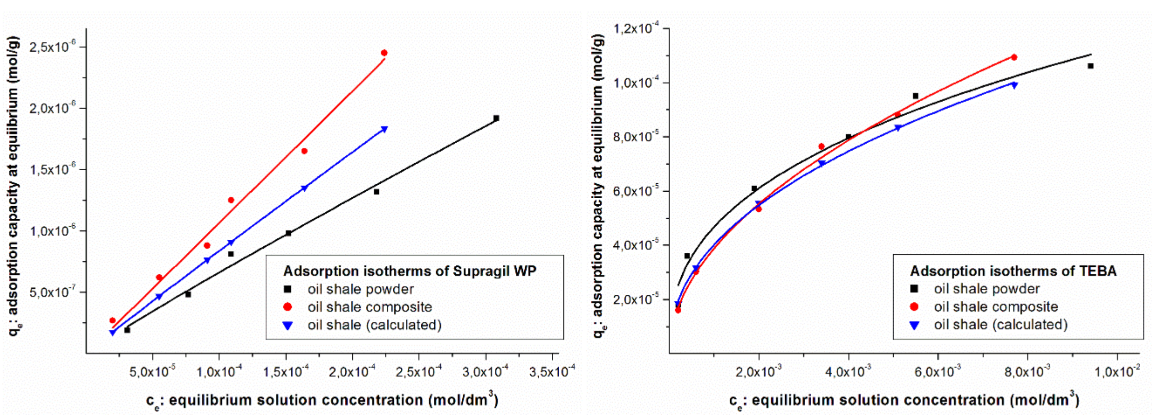

Figure 2. Adsorption isotherms of Supragil WP (left) and TEBA (right)

As can be seen on Figure 2,the adsorbedamount of Supragil WP on oil shale in composite (left, blue line) is higher than that on oil shale powder (left, black line). It can be explained by the difference of liquid-solidratio compared the powder to the composite. Thus, the repulsion between the anionic Supragil WP and the anionic surface-charged oil shale powder is more significant.

In the case of TEBA, the adsorbedamounton oil shale in composite (right, blue line) is lower thanon the powder (right, black line). It can be caused bythe hindered diffusion of cationic TEBA through the negatively charged alginate tothe oil shale.

Conclusion

The adsorption of two widely used asymmetric polar compounds was investigated on Hungarian oil shale powder and its newly synthesized composite form. The extent of adsorptionof anionic Supragil WP as adsorbate on oil shale in the new composite, wasgreater. This result is attributed to the different liquid-solid ratio. Thesame experimentcarried out with cationic TEBA as adsorbate resulted in less adsorbed amount on oil shale than on its composite form. This can be explained by the hindered diffusion of the compound through the alginate adhesive. The results of the present work suggest that the alginate could be a promising material to form a manageable composite for eliminating chemical pollutants efficiently.

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